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Temperature and Salt Effects on the Rate of Depolymerization of Trioxane in Concentrated Hydrochloric Acid Solutions

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The rate of depolymerization of trioxane in aqueous hydrochloric acid has been measured at four temperatures between 30 and 60°, with an acid concentration range between 1 and 9 *M*. The energy of activation is approximately independent of acid concentration and temperature, and the Arrhenius frequency factor for the first order rate constant correlates accurately with the Hammett acidity function, h_0. The first order rate constant can be expressed (in sec.$^{-1}$) by the equation $k = 3.6 \times 10^{13} h_0^{1.18} \exp(-28{,}700/RT)$. The effect on the rate at 40° of adding salts to the reaction mixture has been studied for six salts at a single salt concentration and for lithium chloride over a wide range of salt and acid concentrations. All of the salts increase the rate. The first order rate constant for the HCl–LiCl mixtures at 40° can be expressed as $\log k = -1.16 H_0 + 0.320 c_s - 6.318$, where c_s is the molar concentration of lithium chloride and H_0 is the Hammett acidity function for the salt-free acid solution at 25°.

Introduction

The rates of a number of reactions catalyzed by strong acids at high concentrations have been shown to correlate closely with the Hammett acidity function of the acid medium, H_0.[1] These correlations have been found valuable in the study of the mechanism of acid catalysis. In only a few instances, however, have extensive rate measurements been made for such reactions at more than one temperature[2] or with salts[3] added to the reaction mixture. The present investigation is a study of temperature and salt effects on the rate of depolymerization of trioxane in concentrated hydrochloric acid solutions.

The depolymerization of trioxane is a first order reaction both in the gas phase[4] and in aqueous and non-aqueous solutions of strong and weak acids.[5] Close correlations have been reported between the rate of the acid catalyzed reaction and H_0 at 25[6] and at 40°.[3b,7] According to the Zucker–Hammett hypothesis,[8] these correlations imply that the reaction is of the A-1 type, *i.e.*, that trioxane is protonated rapidly and reversibly, the protonated species then decomposing in a slow unimolecular step, the transition state of which does not contain a water molecule.

The present paper presents results of measurements of the rate of depolymerization of trioxane in aqueous hydrochloric acid solutions at 30, 40, 50 and 60°, the acid concentrations being between 5 and 9 *M* at 30°, 3 and 7 *M* at 40°, 2 and 6 *M* at 50° and 1 and 4 *M* at 60°. Rate constants for the depolymerization are also presented for reaction mixtures containing varying amounts of lithium chloride and acid catalyst, and also for mixtures containing separately NaCl, KCl, NH_4Cl, $(CH_3)_4NCl$ and C_5H_5NHCl, the salt concentrations being 1 *M*, with an acid concentration of 4 *M*.

Experimental

The reaction rates were measured dilatometrically.[7] The dilatometer consisted of reaction vessels of about 60 ml. capacity joined by means of a ground glass joint to a 30 cm. length of capillary tubing (0.6 mm. inner diameter). The reactions were carried out in a water-bath whose temperature was controlled to within 0.005°. Reactants were brought to the temperature of the bath before mixing, and dissolved air was removed from the reaction mixtures by means of a vacuum pump before filling the dilatometer.

At least two runs were carried out for each reaction mixture. Most of the rate constants for duplicate runs agreed to within 1%. For some of the very slow and very fast runs, discrepancies of 6% were tolerated. The first order rate constants were calculated by the method of Guggenheim.[9]

Trioxane (Eastman, practical) was dissolved in enough water to make an approximately one molar solution and any insoluble material was filtered. The hydrochloric acid, pyridine and salts were reagent grade and were used without purification. The trioxane concentration in all kinetic runs was approximately 0.25 *M*.

Results and Discussion

Temperature Effects.—The first order rate constants for the depolymerization of trioxane in aqueous hydrochloric acid solutions at various temperatures are given in Table I.

TABLE I

FIRST ORDER RATE CONSTANTS, ENERGIES OF ACTIVATION AND FREQUENCY FACTORS FOR THE DEPOLYMERIZATION OF TRIOXANE IN AQUEOUS HYDROCHLORIC ACID SOLUTIONS

HCl,	$k \times 10^6$ (sec.$^{-1}$)					E_a	$A \times 10^{-13}$
M	25°[a]	30°	40°	50°	60°	(kcal.)	(sec.$^{-1}$)
1	0.0615	...	....	...	11.3	29.3	6.0
2	.253	...	....	11.1	43.5	28.8	24
3	.678	...	7.68	30.2	118	28.6	66
4	1.75	...	20.0	79.3	303	28.9	170
5	4.70	10.8	52.3	173	...	28.6	440
6	11.8	32.5[b]	136	487	...	28.4	1200
7	....	87.3[c]	367	...	...	28.5	3400
8	.....	282	....	...	...	..	....
9	.....	772	....	...	...	..	....

[a] Rate constants at 25° were interpolated from the data in Ref. 6. [b] (HCl) = 6.07 *M*. [c] (HCl) = 7.05 *M*.

The activation energies, E_a, and frequency factors, A, defined by the Arrhenius equation

$$k = A \exp(-E_a/RT)$$

are also included in Table I. The rate data obtained by Bell, *et al.*,[6] at 25° are in line with the results of the present investigation, even though a

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[1] For recent reviews of the Hammett acidity function and its applications to acid catalysis, see (a) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957); (b) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

[2] (a) P. M. Leininger and M. Kilpatrick, THIS JOURNAL, **60**, 1268, 2891 (1938); (b) P. M. Leininger and M. Kilpatrick, *ibid.*, **61**, 2510 (1939); see also ref. 1b, p. 945.

[3] (a) J. N. Pearce and M. E. Thomas, *J. Phys. Chem.*, **42**, 455 (1938); (b) M. A. Paul, THIS JOURNAL, **74**, 141 (1952); (c) F. A. Long and D. McIntyre, *ibid.*, **76**, 3243 (1954).

[4] R. L. Burnett and R. P. Bell, *Trans. Faraday Soc.*, **34**, 420 (1938).

[5] J. R. Walker and A. F. Chadwick, *Ind. Eng. Chem.*, **39**, 974 (1947).

[6] R. P. Bell, K. N. Bascombe and J. C. McCoubrey, *J. Chem. Soc.*, 1286 (1956).

[7] M. A. Paul, THIS JOURNAL, **72**, 3813 (1950).

[8] See ref. 1b, p. 935–943.

[9] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 428 (1926).

different method of analysis was employed in following the course of the reaction. It will be observed that there is no systematic variation in the activation energy with concentration of HCl. The frequency factors in Table I were calculated using the average value of E_a (28.7 kcal./mole) and the values of k at 45° read from the Arrhenius plots of log k *vs.* $1/T$. A plot of log A against H_0[10] measured at 25° gives a straight line of slope −1.18, the equation for this line being

$$\log A = 13.562 - 1.18\, H_0$$

where A is in sec.$^{-1}$. The first order rate constant then can be expressed as

$$k = 3.6 \times 10^{13}\, h_0^{1.18} \exp\left(-\frac{28{,}700}{RT}\right)$$

where $H_0 = -\log h_0$. In logarithmic form

$$\log k = 13.562 - 1.18\, H_0 - \frac{6260}{T}$$

The accuracy with which this equation represents the available data can be seen from a plot of log k against $1.18\,H_0 + 6260/T$, as shown in Fig. 1.

Plots of log k against H_0 for the various temperatures gave straight lines, the slopes of which are given in Table II. No systematic variation in slope is observed, the average value being 1.17.

TABLE II

SLOPES OF LOG K–H_0 PLOTS AT VARIOUS TEMPERATURES FOR THE DEPOLYMERIZATION OF TRIOXANE IN AQUEOUS HYDROCHLORIC ACID

Temp., °C.	$\frac{d(\log k)_t}{d(H_0)_{25°}}$
25	−1.18[a]
30	−1.18
40	−1.16
50	−1.16
60	−1.18

[a] Calculated from data in ref. 6.

(For the measurements at 30°, the best straight line was drawn through the points corresponding to HCl concentrations of 5, 6 and 7 M, since it is commonly observed that log k is linear with H_0 for HCl solutions only up to an acid concentration of 7 M.[11])

These results may be compared with those obtained from similar measurements of the rate of hydrolysis of sucrose and of ethylal in hydrochloric acid solutions.[2] These reactions also correlate with H_0 at a given temperature.[1b] However, the experimental activation energies depend on both the acid concentration and the temperature, and consequently the slope, $d(\log k)/d(H_0)_{25°}$, changes with temperature.

The results of the present investigation can be interpreted in terms of the A-1 mechanism proposed for reactions that are found to correlate with H_0. This mechanism may be formulated as

$$F_3 + H^+ \rightleftharpoons F_3H^+ \quad \text{(equilibrium)}$$
$$F_3H^+ \rightleftharpoons M^+ \longrightarrow 3F + H^+ \text{(slow)}$$

F represents a molecule of formaldehyde and M^+ the transition state of the rate determining step.

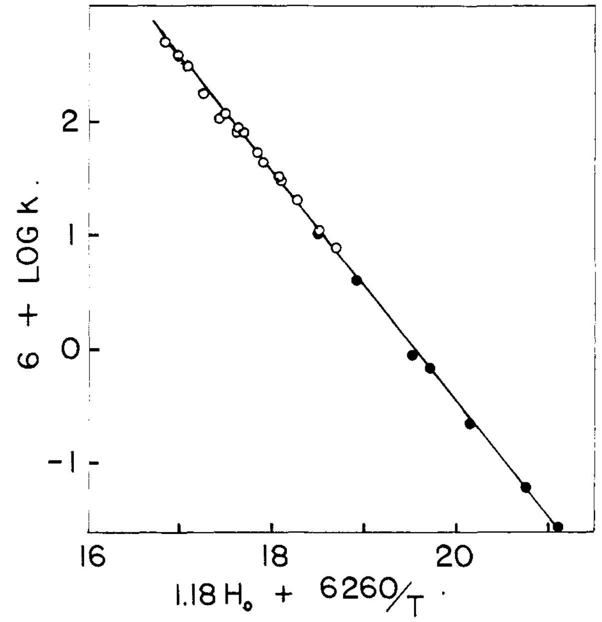

Fig. 1.—The rate of depolymerization of trioxane in aqueous hydrochloric acid solutions as a function of H_0 and the temperature: ○, this work; ●, Bell, *et al.*, ref. 6.

The Brönsted equation for medium effects on the first order rate constant is

$$\log k = \log k_0 + \log a_{H^+} \frac{f_{F_3}}{f_{M^+}} \qquad (1)$$

where k_0 is a constant independent of acid concentration, a_{H^+} is the hydrogen ion activity and the f's are activity coefficients taken to be unity in infinitely dilute solution. Addition of $H_0 = -\log a_{H^+} f_B/f_{BH^+}$ to the above equation and then rearrangement of terms gives

$$\log k = \log k_0 - H_0 + \log \frac{f_{F_3} f_{BH^+}}{f_{M^+} f_B} \qquad (2)$$

Log k will be linear with $-H_0$ with unit slope at all temperatures only if the activity coefficient ratio in equation 2 is identically equal to one at all acid concentrations and temperatures. The above results indicate that this ratio is concentration dependent but that it is independent of temperature in the range 25–60°. The corresponding term in the analogous equation for the hydrolysis of sucrose and of ethylal, however, apparently depends both on acid concentration and on temperature. This accounts for the concentration and temperature dependence of the experimental activation energy for these reactions.

It is of interest to compare the rate constant for the acid catalyzed depolymerization of trioxane corrected for medium effects, k_0, with the specific rate of the homogeneous gas phase reaction, k_g.[4]

$$k_g = 1.5 \times 10^{15} \exp\left(-\frac{47{,}400}{RT}\right)$$
$$k_0 = 3.6 \times 10^{13} \exp\left(-\frac{28{,}700}{RT}\right)$$

The reaction in acid solution has both a lower activation energy and a lower frequency factor and therefore a lower entropy of activation.

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(10) All values of H_0 referred to in this paper were taken from Table II, page 12, of ref. 1a. For acid concentrations greater than 6 M, the corrected values of H_0 given on the same page were used.

(11) Ref. 1b, p. 956.

Salt Effect.—The influence of salts on the hydrochloric acid catalyzed depolymerization of trioxane at 40° was studied for six different salts. For each kinetic run the acid concentration was 4 *M* and the salt concentration 1 *M*. The ratios k_s/k are given in Table III, where k_s and k are the rate constants for the salt mixture and the salt free mixture, respectively. The corresponding ratios for the hydrochloric acid catalyzed hydrolysis of sucrose[3a] and of methylal[3c] at 25° are included for comparison. In each case the rate is increased by addition of salt, the salts with the smaller cations being the most effective. It is also interesting to note that the magnitude of the salt effect decreases with increasing size of the molecule undergoing decomposition; *i.e.*, sucrose < trioxane < methylal.

TABLE III

SALT EFFECTS ON THE RATES OF SOME HYDROCHLORIC ACID CATALYZED REACTIONS

	k_S/k		
Salt (concn. = 1 *M*)	Trioxane depolymeriz. at 40° (HCl) = 4 *M*	Sucrose[a] hydrolysis at 25° (HCl) = 1 *M*	Methylal hydrolysis at 25° (HCl) = 0.371 *M*
LiCl	2.12	1.44	2.6
NaCl	1.87	1.39	2.3
KCl	1.50	1.33	2.1
NH_4Cl	1.50	..	..
$N(CH_3)_4Cl$	1.23	..	..
C_5H_5NHCl	1.47	..	..

[a] Salt concentrations are 1 molal.

According to the Brönsted equation for medium effects on the first order rate constant (equation 1), changes in *k* due to the presence of salts in the reaction mixture depend upon the influence of the salt upon the ratio $a_{H^+}f_{F_t}/f_{M^+}$. In the case of the hydrolysis of methylal,[3c] Long and McIntyre showed that salt effects on the activity coefficient of methylal (corresponding to f_{F_t} in the present study) do not parallel the changes produced on the rate constant; hence for this reaction the ratio a_{H^+}/f_{M^+} must also vary with salt concentration.

The salt effect of lithium chloride was studied over a wide range of acid and salt concentrations. The rate constants for the various reaction mixtures are given in Table IV. It was found that the logarithm of the rate constant varies linearly with the salt concentration, the slope being independent of the acid concentration. Thus

$$\log k = -1.16H_0 + 0.320c_s - 6.318 \qquad (3)$$

where c_s is the molar concentration of the salt and H_0 is the acidity function for the salt free acid solution.

TABLE IV

RATE CONSTANTS FOR THE DEPOLYMERIZATION OF TRIOXANE IN AQUEOUS HCl–LiCl MIXTURES AT 40°

HCl, *M*	LiCl, *M*	$k \times 10^6$ (sec.$^{-1}$) (exptl.)	$k \times 10^6$ (sec.$^{-1}$) (calcd., eq. 3)
2	5	125	120
3	0	7.68	8.0
3	1	14.8	16.6
3	4	135	151
4	0	20.0	20.0
4	1	44.5	41.7
4	2	90.3	87.0
4	3	197	182
4	4	467	380
5	0	52.3	52.5
5	1	108	110
5	2	247	229
6	0	136	138
6	1	278	288

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Rate Processes and N.m.r. Spectra. III. Proton Exchange and Hydrolysis of Amides[1]

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The chemical exchange of the NH protons in pure liquid N-methylformamide (NMF) and N-methylacetamide (NMA) and the hydrolysis of the compounds in acid solution have been studied by high resolution proton magnetic resonance methods. The activation energy required for exchange among the NH protons is found to be 14 ± 2 kcal. mole^{-1} for both NMF and NMA. The rate constants of the acid hydrolysis were determined at three different temperatures, giving activation energies of 13 ± 3 and 15 ± 3 kcal. mole^{-1} for the hydrolysis of NMF and NMA, respectively. The relationship between the proton exchange and the acid hydrolysis is discussed, and it is proposed that the N-protonated form of the amides is that which undergoes the acid hydrolysis.

Introduction

A high resolution nuclear magnetic resonance (n.m.r.) spectrum exhibits fine structure as a result of chemical shifts and the electron coupling of nuclear spins.[3] These components are usually narrow because the random molecular tumbling in the liquid or gaseous state averages out the direct magnetic interaction between the nuclear spins.[4] However, the high resolution fine structure may in turn be broadened or averaged out by rate processes, in particular by the exchange of nuclei between chemically non-equivalent sites or among the sites in which nuclei experience the indirect spin-spin coupling. The possibility of evaluating the rate constants and activation energies for such processes was pointed out in the first paper of this series.[5]

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[2] On leave of absence from Himeji Technical College, Himeji, Japan. Reprints of this article may be obtained from H. S. Gutowsky.

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[4] N. Bloembergen, E. M. Purcell and P. V. Pound, *Phys. Rev.*, **71**, 466 (1947).

[5] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953). Hereafter called Paper J.